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## **Final Report**

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“Bulk Metallic Glass Matrix Composites”  
Dept. of Materials Science  
California Institute of Technology  
August , 1998**

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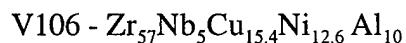
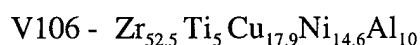
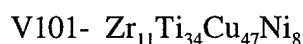
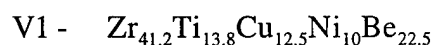
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## Summary/Overview

The present document is a final report on research project carried out during the three year period May 15, 1995 through May 14, 1998 under sponsorship of the U.S. Army Research Office under grant No. DAAH04-95-0233 entitled "Bulk Metallic Glass Matrix Composites". The report was prepared by the principal investigator, Prof. William L. Johnson, Mettler Professor of Materials Science, Dept. of Materials Science, California Institute of Technology, Pasadena, CA. The grant was initiated in 1995 for the purpose of developing synthesis and processing methods to produce bulk metallic glasses reinforced with both ductile metal and ceramic reinforcement materials. A companion STIR program (Grant DAAG55-97-1-0287 from ARO) was carried out in 1997 in parallel with the present project.

BMG/matrix composites were synthesized using four types of bulk metallic glass forming alloys, Zr-Ti-Ni-Cu-Be (Vitreloy 1 or V1), Zr-Ti-Ni-Cu (V101), Zr-Ti-Ni-Cu-Al (V105) and Zr-Nb-Ni-Cu-Al (V106) as the matrix materials for the composites. The exact compositions (in atomic %) of the four bulk metallic glass forming alloys used in this study are:



. These metallic glasses were combined with several types of second phase reinforcement materials. The reinforcements were introduced in the form of particulates, short fibrils, and long/continuous fibers, and porous preforms. The reinforcement materials fall into two categories: 1) ductile metals, and 2) refractory ceramics. Ductile metal reinforcements include steel, tungsten, and tantalum. Ceramic reinforcements included SiC, carbon fiber, WC, and TiC. A summary of the composites which were successfully synthesized with a metallic glass matrix is included in Table I.

Mechanical properties of several types of composites were evaluated. Quasistatic tensile and compressive yield strength were measured using a standard hydraulic load frame on both ductile metal reinforced and ceramic reinforced composites. Charpy impact measurements were carried out for ductile metal reinforced composites. Three point bend testing of notched samples was used to evaluate the plane strain fracture toughness of the pure metallic glass and of several composites. Split Hopkinson bar tests, and ballistic testing were used to determine and characterize the dynamic deformation behavior of the bulk metallic glass itself. Similar experiments were carried out to examine the dynamic failure behavior of BMG/tungsten composites.

The BMG/tungsten composites were evaluated as potential kinetic energy penetrator materials under support by a supplementary 6 month STIR program (DAAG55-97-1-0287) . A copy of the final report for the STIR program is attached to this report for reference and includes comparative penetration data for BMG/tungsten composite vs. convention tungsten-heavy or WHA alloys.

Two U.S. patents were filed based on results of research carried out under this project. These include:

- 1) "Ductile Reinforced Amorphous Metal Product and Method", (Caltech Ref. No. CIT2532) filed at the USPTO in 1997.
- 2) "Kinetic Energy Penetrator Containing Bulk Metallic Glass", filed in 1997.

**Table I. Overview of composite synthesis studies to date. Particulate samples in form of cast 4x6 mm bars. Wire and Monofilament reinforced samples in form of 0.25 - 0.5" diameter rods or 4x6 mm bars. A=amorphous matrix, X=crystalline or partially crystalline matrix.**

<b><u>Glassy Matrix\</u></b> <b><u>Reinforcement</u></b> <b><u>&amp; Composite</u></b> <b><u>Type/</u></b>	<b>V1</b>	<b>V101</b>	<b>V105</b>	<b>V106</b>
<b><u>Particulate</u></b>				
<b>-10-20% SiC</b>	A	A	A	A
<b>-30% SiC</b>	-----	A	X	X
<b>-5% WC</b>	-----	X	A	A
<b>-10% WC</b>	-----	X	X	A
<b>-15% WC</b>	-----	X	X	A
<b>-10% diamond</b>	A	-----	-----	-----
<b>-10 % TiC</b>	-----	A	X	A
<b>-5-10% tungsten</b>	A	A	A	A
<b>-15% tungsten</b>	A	X	X	A
<b>-10% tantalum</b>	A	-----	-----	A
<b><u>Fibers, Fibrils,</u></b> <b><u>Monofilaments</u></b>				
<b>-SiC</b>	A	-----	-----	-----
<b>-carbon fiber</b>	A	A	-----	-----
<b>-steel wire</b>	A	-----	-----	-----
<b>-tungsten wires</b> <b>(up to 80 %)</b>	A	A/X	A	A
<b>-titanium wire</b>	A/X	X	-----	-----
<b><u>Infiltrated</u></b> <b><u>Ceramic Preform</u></b>				
<b>-SiC preform</b>	A	-----	-----	-----
<b>-porous graphite</b>	A	-----	-----	-----
<b>-carbon fiber</b>	A	-----	-----	-----

## **Project Participants**

The following is the list of personnel who were partially supported or support in full by the grant during the three year performance period. The periods of participation are indicated. Professor Goddard's participation as a co-investigator was primarily as a co-supervisor of Dr. Mo. Li and through the use of his computational facilities. Computer simulation work was carried out during the first year of the project by Mo Li in Professor Goddard's "Materials Simulation Laboratory".

1. Professor William L. Johnson, Mettler Professor of Materials Science, Calif. Inst. of Tech., **Principal Investigator**
2. Professor William A. Goddard, Merkel Professor of Chemistry, Calif. Inst. of Tech., **Co-Principal Investigator**
3. Dr. Mo Li, Post Doctoral Fellow in Materials Science, participated part time in 1995 -96
4. Robert Dale Conner, Graduate Student in Materials Science, participated full time, 1995-98, (Ph.D. completed in December 1997)
5. Richard Dandliker, Graduate Student in Materials Science, participated full time, 1995-97, (Ph. D. completed in November 1997)
6. Haein Choi-Yim, Graduate Student in Materials Science, participated full time, 1995-98, (Ph.D. expected in September 1998)
7. Dr. Valerie Scruggs, Post Doctoral Fellow in Materials Science, participated 1997-present (8 months, part time)
8. Dr. Ulrich Geyer, Post Doctoral Fellow in Materials Science, participated during the year 1995, partially supported under this grant (carried out atomic diffusion measurements in the metallic glass matrix materials)

## Publications/ Patents

The following technical manuscripts were published or submitted for publication in the open literature based on the work supported by this grant. Two of the publications/patents (#11 and #14 below) were primarily supported under the companion STIR grant -DAAG55-97-1-0287 and only secondarily supported by the present grant. The list of publications includes two Ph.D. theses submitted at Caltech along with two patents which were filed with the U.S. Patent Office. The Patents are listed separately at the end of the section below.

1. H. Choi-Yim, R. Busch, and W.L. Johnson, "The effect of silicon on the glass forming ability of the  $\text{Cu}_{47}\text{Ti}_{34}\text{Zr}_{11}\text{Ni}_8$  bulk metallic glass forming alloy during processing of composites", J. of Appl. Phys., **83**, No. 12 (June 1998)
2. H. Choi-Yim and W.L. Johnson, "Bulk metallic glass matrix composites", Appl. Phys. Lett., **71**, 3808 (1997)
3. R. Dandliker, R.D. Conner, and W.L. Johnson, "Melt infiltration casting of bulk metallic glass matrix composites", J. Mater. Res., **13**, No. 6 (June 1998)
4. U. Geyer, S. Schneider, Y. Qiu, T.A. Tombrello, and W.L. Johnson, "Small atom diffusion in the glassy and supercooled liquid states of bulk amorphous Zr-Ti-Ni-Cu-Be alloys", Mater. Sci. Forum, **235-238**, 343 (1997)
5. Y. Qiu, U. Geyer, W. Schneider, W.L. Johnson, and T.A. Tombrello, "Investigation of Beryllium Diffusion in the Supercooled Liquid and Glassy States of the Amorphous Alloy  $\text{Zr}_{41.25}\text{Ti}_{13.75}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$  by High Energy Helium Elastic Backscattering", Nucl. Inst. Meth. B, **117**, 151 (1996)



6. R.D. Conner, R.B. Dandliker, and W.L. Johnson, "Mechanical properties of tungsten and steel fiber reinforced  $Zr_{41.25}Ti_{13.75}Cu_{12.5}Ni_{10}Be_{22.5}$  metallic glass matrix composites", submitted to Acta Materialia (April 1998)

7. R.D. Conner, H. Choi-Yim, and W.L. Johnson, "Mechanical properties of  $Zr_{37.5}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$ , metallic glass matrix particulate composites", submitted to J. of Mater. Res., (April 1998)

8. R.D. Conner, "Mechanical Properties of Bulk Metallic Glass Matrix Composites", Ph.D. Thesis, California Institute of Technology, submitted Oct. 28, 1997

9. R.B. Dandliker, "Bulk Metallic Glass Matrix Composites: Processing, Microstructures, and Application as a Kinetic Energy Penetrator", Ph. D. Thesis, California Institute of Technology, submitted Oct. 24, 1997

10. M. Li, W.L. Johnson, and W.A. Goddard, "Evidence of Hexatic Phase Formation in Lennard Jones Binary Arrays", Phys. Rev. B, **54**, 12067 (1996)

11. R.D. Conner, R.B. Dandliker, V. Scruggs, and W.L. Johnson, "Dynamic Deformation Behavior of Tungsten-fiber/ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  Metallic Glass Matrix Composites", submitted to J. Dynamic Deformation, July (1998)  
**(primary support for this work was provided under the STIR grant - DAAG55-97-1-0287, partial support was provided under the present grant. Specifically, ballistic testing work was provided by the STIR grant.)**

12. H. Ikeda, Y. Qi, T. Cagin, K. Samwer, W.L. Johnson, and W.A. Goddard III, "Strain Rate Induced Amorphization in Metallic Nanowires", submitted to Phys. Rev. Lett., August 1998

## **Patents / Inventions**

13. R.D. Conner, R.B. Dandliker, H. Choi-Yim, and W.L. Johnson "Ductile Reinforced Amorphous Metal Product and Method", U.S. Patent Application, filed May 1997 (Caltech Ref. No. CIT 2532)

14. R. D. Conner, R.B. Dandliker, M. Tenhover, and W.L. Johnson, "Kinetic Energy Penetrator Containing Bulk Metallic Glass", U.S. Patent Application, filed Sept. 1997  
**(primary support for this work was provided under the STIR grant - DAAG55-97-1-0287, partial support was provided under the present grant)**

# Highlights and Accomplishments

## Synthesis and Processing

Bulk metallic glass matrix composites were fabricated by two primary methods as follows:

### -Direct Casting

Direct inclusion of relatively small volume fractions (up to 30 volume %) of the reinforcement phase into the molten glass forming alloy followed by casting of the liquid/solid mixture into metal molds.

### -Melt infiltration

Preforms consisting of bundles of wires or fibers, or sintered porous preforms (e.g. sintered SiC preforms) are first heated to a processing temperature and then subsequently infiltrated by capillary action by the molten glass forming alloy. The infiltrated mixture is then quenched to low temperature to retain the glassy structure of the solidified matrix.

Composites were successfully fabricated by both types of methods as described in Table I above. The direct casting technique is described in **references 1-3,7, 8 and 9** in the previous section. The infiltration method is described in **references 3,6,8, and 9**. It has been clearly demonstrated that BMG/matrix composites with a variety of glass forming matrix alloys and reinforcement materials can be formed using these processes.

## Mechanical Properties

Quasistatic mechanical testing of both the bulk metallic glasses and the BMG composites in compression and tension has been carried out. BMG/tungsten, BMG steel, BMG/SiC, and BMG/WC composites were evaluated as described in **references 6-8**. The metallic glass alloys are typically strong (yield strength of ~2Gpa) and sustain large elastic strains (~2%) prior to yielding, but fail catastrophically along narrow shear bands. Reinforcement by both ceramic particles and ductile metals have been found to increase the plastic strain to failure and the toughness of the materials. For example, compressive strain

to failure was increased by over 300% in particulate composites reinforced with W and WC particles (see refs. 7 and 8). The increase in toughness is attributed to the particulate reinforcement restricting the propagation of shear band, promoting the generation of multiple shear bands, and increasing the fracture surface area.

Continuous reinforcement with tungsten wires increased the compressive strain to failure by over 900% compared to the unreinforced amorphous metal as described in references 6-8. Samples reinforced with continuous steel wire had increased strain to failure in tension and increased energy to breaking of 13-18 %. Tensile toughness is increased as a result of ductile fiber delamination, fracture, and fiber pull-out.

In BMG/tungsten composites containing varying volume fractions of continuous uniaxial tungsten wire as reinforcement, the yielding and failure of the samples was studied in both compression and tension. The formation of multiple shear bands at an angle of 45 degrees to the compressive axis remains the dominant mode of compressive failure in composites containing less than 50% tungsten wire. For higher volume fractions of W, a tilting and buckling failure mode is observed at quasistatic strain rates.

BMG/tungsten composites were studied under dynamic deformation conditions at high strain rates using split Hopkinson bar tests and ballistic impact testing. Compressive failure by 45 degree shear banding becomes the dominant failure mode in all composites (containing up to 80 volume % tungsten) at the highest strain rates of  $10^5 \text{ s}^{-1}$  or higher. This led to evaluating the BMG/tungsten wire reinforced composites as kinetic energy penetrators.

### **Application as Kinetic Energy Penetrators**

The tendency of BMG/tungsten composites to failure by multiple shear banding at 45 degrees to the compressive axis (aligned with the tungsten wires) suggests application of these materials as kinetic energy penetrators (KEP's). The formation of localized adiabatic shear bands under dynamic compressive loading along directions of maximum resolved shear stress is believed to be an important factor in performance of KEP's. This mode of yielding and failure results in self sharpening behavior of the penetrator. Since metallic glasses are prone to formation of localized adiabatic shear bands during deformation, it was expected that the BMG/tungsten composites would be interesting candidate materials for penetrators.

Towards this end, we submitted a separate STIR proposal to ARO to provide additional resources to carry out ballistic testing on BMG/tungsten composites. This project

was funded by ARO (Grant No. DAAG55-97-1-0287). As a bench mark, we obtained samples of currently used "tungsten heavy alloys" (WHA) from Dr. Robert Dowding of the Army Research Laboratory in Aberdeen. Ballistic testing was carried out in a 35mm gas gun at Caltech using a sabot assembly to launch 0.25" diameter rods (right circular cylinders) with lengths of 1.5" or 2.0" into targets of 6061 aluminum alloys and 4130 heat treated steel (a material used as a model for roll hardened armor). Impact velocities ranging up to 1300 m/s were used and a comparative penetration study was carried out for the BMG/tungsten and WHA materials. The penetration results show that the BMG/tungsten composite materials exhibits superior penetration into both types of target materials. The results are summarized in **ref. 11** (see above) and also in the attached final report for the STIR project.

## Simulation

In a collaborative project between the research groups of Profs. Goddard and Johnson, we have developed molecular dynamic codes for the simulation to binary metallic glass forming alloys. During the early stages of the work sponsored by this project, Dr. Mo Li was partially supported by the present grant to participate in the development of these computer simulation codes. **Ref. 10** describes work carried out by Li on the simulation of binary Lennard Jones alloys.

The MD collaborative work, with the group of Prof. Goddard at the Caltech Materials Simulation Center, is currently under further development. Prof. Johnson (supported under the present grant), Dr. Hideyuki Ikeda (visiting professor on sabbatical leave 1997-1998), have been carrying out MD simulation of the deformation behavior of nanowires under tensile and compressive loading conditions. Both amorphous and crystalline (fcc) wires are being studied. Numerous results have been obtained. First, it has been found that under deformation at high strain rates, the crystalline nanowires (Nickel, Copper, and fcc alloys) show cooperative twinning and ultimately transformation to the amorphous phase as the strain rate (tensile strain) is increased (see **ref. 12** above). This work has allowed us to identify transitions from dislocation slip, to twinning, and ultimately to amorphization, as the mechanisms of deformation in crystals with progressively increasing strain rate. Basically, there is an ultimate strain rate which can be sustained by crystalline samples. Beyond this rate, the crystal develops shear instability and "melts" to an amorphous phase. The amorphous phase, in turn, can sustain higher strain rates. Amorphous alloy wires (Au-Ni and Cu-Ni alloys) produced by melting and quenching have also been deformed at high strain rates from  $10^8$  to  $10^{11}$  per sec. to

obtain the stress/strain rate constitutive relation (in this range of strain rates). This yields the strain rate sensitivity, and other characteristics of the deformation behavior in the amorphous phase at high strain rates. We plan to further extend this work to determine the "work hardening", "strain rate hardening", and "thermal softening" behavior of metallic glasses with the goal of developing an analytical model of shear localization and formation of localized shear bands in bulk metallic glasses. This work is in the early stages and will be the subject of further investigation in under the continuation proposal submitted as a follow on to the present grant.

6. R.D. Conner, R.B. Dandliker, and W.L. Johnson, "Mechanical properties of tungsten and steel fiber reinforced  $\text{Zr}_{41.25}\text{Ti}_{13.75}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$  metallic glass matrix composites", submitted to Acta Materialia (April 1998)

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